Preface

In the first chapter a brief description of molecular magnetic system is given. We have discussed the origin of exchange interaction which controls the magnetic behaviour in molecules and solids. Various microscopic electronic Hamiltonians have been introduced and relation to spin Hamiltonian is described. Various computational methods for solving quantum many body problems are introduced such as the exact diagonalization technique in valence bond and constant M_S basis which are employed in this thesis for studying magnetic nanoclusters and molecular magnets. Brief descriptions of density matrix renormalization group and quantum Monte Carlo method, which are widely used for studying large systems, are given.

Single molecule magnets like $Mn_{12}Ac$, Fe_8 have high spin ground state, large anisotropy and negligible intermolecular interaction. They exhibit quantum effects like resonant tunneling, quantum interference at a macroscopic level. To understand these phenomena, we have investigated the low-lying spectra and quantum dynamics in the $Mn_{12}Ac$ cluster in the second chapter. Beginning with a Heisenberg exchange Hamiltonian for the manganese ions in the $Mn_{12}Ac$ molecule, we have found a number of model exact low-energy states of the system. We have fitted the exchange constants of the system by comparing the theoretical level ordering and the energy gap to that proposed from experiments. Starting with the initial state ($S = 10$, $M_S = -10$), we find the evolution of magnetization under the influence of a spin Hamiltonian involving dipolar interactions and external magnetic fields. Magnetization response to time varying external field is computed by solving the time-dependent Schrodinger equation. The external fields introduced were ramped magnetic field applied axially, strong sinusoidal axial field both with and without a weak static transverse field. These studies were confined to zero temperature.

V_{15} is a magnetic cluster made up of 15 spin-1/2 V^{4+} ions and is known to have ground

state spin 1/2. Since the ground state spin is 1/2, it can not exhibit resonant tunneling in the ground state spin manifold and it is thus different from the high spin clusters Mn_{12} and Fe_8. Nonetheless, hysteresis is observed when a magnetic field is swept at a slow rate (of the order of few tenths of Tesla per second) at low temperatures and the hysteresis is known as 'butterfly' hysteresis because of its shape. To understand this phenomena, in the third chapter we have studied the quantum dynamics of V_{15} in the presence of spin-spin and spin-phonon interaction. We have also studied the effect of Dzyaloshinskii-Moriya (DM) interaction on the energy level structure of V_{15}. Starting from an antiferromagnetic Heisenberg Hamiltonian for the 15 spin-1/2 ions in V_{15}, we have constructed an effective Hamiltonian involving eight low-lying states coupled to a phonon bath. We have numerically solved the time-dependent Schrödinger equation of this system and obtained the magnetization as a function of temperature in a time-dependent magnetic field. The magnetization exhibits unusual patterns of hysteresis and plateaus as the field sweep rate and temperature are varied. The observed temperature dependence of the plateau width is reproduced by our model. We have studied the low energy structure of the V_{15} using exact diagonalization method in the presence of DM interaction. We find that the DM exchange interaction leads to an energy gap which has also been found experimentally. Adiabatic changes of the magnetization with the sweeping field are also investigated in this model.

Ferric wheels are made up of Fe^{3+} ions which form antiferromagnetic ring structure. They belong to the class of single molecule magnets with low-spin ground state. They exhibit interesting spin-dispersion and excited state dynamics. In the fourth chapter, using an efficient numerical scheme that exploits spatial symmetries and spin-parity, we have obtained the exact low-lying eigenstates of exchange Hamiltonians for ferric wheels up to Fe_{12}. The largest calculation involves the Fe_{12} ring which spans a Hilbert space dimension of about 145 million for the M_s=0 subspace. Our calculated gaps from the singlet ground state to the excited triplet state agrees well with the experimentally measured values. Study of the static structure factor shows that the ground state is spontaneously dimerized for ferric wheels. We

have studied the quantum dynamics of Fe_{10} as a representative of ferric wheels. We use the low-lying states of Fe_{10} to solve exactly the time-dependent Schrödinger equation and find the magnetization of the molecule in the presence of an alternating magnetic field at zero temperature. We observe a nontrivial oscillation of the magnetization which is dependent on the amplitude of the *ac* field. We have also studied the torque response of Fe_{12} as a function of a magnetic field, which clearly shows spin-state crossover.

In the fifth chapter, we examine the low-energy properties of a chain of antiferromagnetically coupled triangles of half-odd-integer spins. We derive the low-energy effective Hamiltonian to second order in the ratio of the coupling J_2 between triangles to the coupling J_1 within each triangle. We compare the results obtained by exact diagonalization of the effective Hamiltonian with those obtained for the full Hamiltonian using exact diagonalization and the density-matrix renormalization group method. It is found that the effective Hamiltonian is accurate only for the ground state for rather low values of the ratio J_2/J_1 and that too for the spin-1/2 case with linear topology. We have also studied the low-energy properties of Heisenberg antiferromagnetic spin-1/2 and spin-1 systems on various clusters made up of triangles. While the ground state always has the lowest possible spin (0 or 1/2), the nature of the low-energy excitations depends on the geometry and the site spin. For the Kagome clusters with spin-1 sites, the lowest excitations are gapped, with singlet and triplet excitations having similar gaps. This is in contrast to Kagome clusters with spin-1/2 sites where there are several low-energy singlet excitations (possibly gapless in the thermodynamic limit), while triplet excitations have a gap. For the sawtooth chain with spin-1 sites, the lowest excitations are triplets with a gap; the gap to singlet excitations is about twice the triplet gap.

Rare-earth(Ln(III))-Cu(II) molecular complexes show interesting magnetic behaviours depending on the nature of the rare-earth atom. Recently, many transition metal and rare-earth complexes have been synthesized with organic radicals like nitronyl nitroxide. To study their magnetic properties in detail in the sixth chapter we have employed a microscopic model hamiltonian which includes electron correlation and spin orbit interaction. We

have obtained the phase diagram of the transition metal-radical complex in the phase space of inter-orbital repulsion parameter U_{dd} and site energy of the radical sp^2 carbon. We have observed that the ground state undergoes a low spin (antiferromagnetic) to high spin (ferromagnetic) transition. In case of half-filled rare-earth radical complex we have found a reentrant low-spin phase when inter-orbital repulsion parameter U_{ff} is increased. This provides an explanation for observing ferro as well as antiferromagnetic interaction in various Gd(III)-radical complexes.